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WATER QUALITY CRITERIA: FOR SELECTED PARAMETERS IN THE RECEIVING WATERS SUISUN BAY, CALIFORNIA, IN THE VICINTY OF THE WASTE DISCHARGE OF THE PHILLIPS PETROLEUM COMPANY, AVON REFINERY, CONTRA COSTA COUNTY, CALIFORNIA

Federal Water Pollution Control Administration
San Francisco, California

October 1966

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WATER QUALITY CRITERIA

For Selected Parameters In The Receiving Waters
Suisun Bay, California, In The Vicinity Of
The Waste Discharge Of The

PHILLIPS PETROLEUM COMPANY

Avon Refinery
Contra Costa County, California

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UNITED STATES DEPARTMENT OF THE INTERIOR

Federal Water Pollution Control Administration
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UNITED STATES DEPARTMENT OF THE INTERIOR
Federal Water Pollution Control Administration
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San Francisco, California
October 1966

This report on Water Quality Criteria has been prepared as a technical consultation to United States Attorney, Cecil F. Poole; John F. Meadows and Henry Haugen, Attorneys, Department of Justice, 450 Golden Gate Avenue, San Francisco, California

Requests for additional information on report contents should be addressed to:

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San Francisco, California
October 21, 1966

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CONSULTANTS AND REGIONAL STAFF

The water quality criteria recommended for the receiving waters of Suisun Bay, in the vicinity of the waste discharge of the Avon Refinery, Phillips Petroleum Company, are the result of extensive consultation. The Regional Staff report coordinator, Regional Staff members and recognized experts in other offices of the Federal Water Pollution Control Administration, pooled their efforts to reach a consensus on the criteria values, analytical procedures, hydraulic review of the proposed deep-water outfall design, and a monitoring program. Consultants and staff members met with representatives of the Phillips Petroleum Company, United States Department of Justice personnel, and the professional staff members of the San Francisco Bay Regional Water Quality Control Board and the California State Department of Fish and Game. Two field visits were made to the Avon Refinery.

In November 1965 representatives of the above mentioned agencies, along with their counterparts from the Bureau of Sport Fisheries and Wildlife, Department of the Interior, met in San Francisco to review the data prepared by the Regional Staff report coordinator. This discussion produced material for a preliminary and revised (February 23, 1966) draft of water quality criteria which in turn was subject to an intensive review at the office of the industrial waste consultant (Cincinnati, Ohio) the week of May 9, 1966.

Following is a list of consultants, agency personnel, and Regional Staff members having major responsibilities for the water quality criteria presented herein.

Consultants

Industrial Wastes

Mr. Hayse H. Black, Chief (Retired May 31, 1966)
Water, Sewage and Industrial Wastes
Technical Advisory and Investigations Activity
Technical Services Program
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Oils and Oily Wastes

Dr. Aaron A. Rosen, Chemist
Organic Contaminants Unit
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State of California

San Francisco Bay Regional Water Quality Control Board

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State of California (Cont'd)

Department of Fish and Game, Region 3

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United States Department of the Interior
Federal Water Pollution Control Administration
Southwest Regional Office

Mr. William B. Schreeder, Regional Director

Mr. James C. McCarty, Staff Sanitary Engineer

Mr. Irving M. Terzich, Staff Sanitary Engineer, Report Coordinator

INTRODUCTION

General

The Avon Refinery of Phillips Petroleum Company is located in Contra Costa County, California, adjacent to Suisun Bay. Suisun Bay (Figures 1 and 2)[1/] forms the easternmost link of the greater San Francisco Bay complex with the inflowing Sacramento-San Joaquin River system. The Company's facilities are astride the railroad tracks at Avon; sea-going tankers unload crude stock at Avon Pier. The major wasteway of the industrial facility is identified as the East Canal, through which wastes are discharged above the water surface (on tidal flats) near the junction of Avon Pier with the shoreline.

Beneficial Uses - Suisun Bay Waters

The waters of Suisun Bay, in the vicinity of the waste discharge, are considered brackish in character. Chloride concentration generally ranges from 0.1 to 10.0 g/l, although during low tides and high fresh-water inflow, and high tides and low fresh-water inflow, Bay waters will exhibit chloride limits respectively lower and higher than those indicated above.

1/ Figure 1 is a reproduction of a section of a common road map of the area. Figure 2 is a reproduction of the site area as shown on Coast and Geodetic Survey Chart No. 5534, "Suisun Bay," 27th Edition, March, 1964.

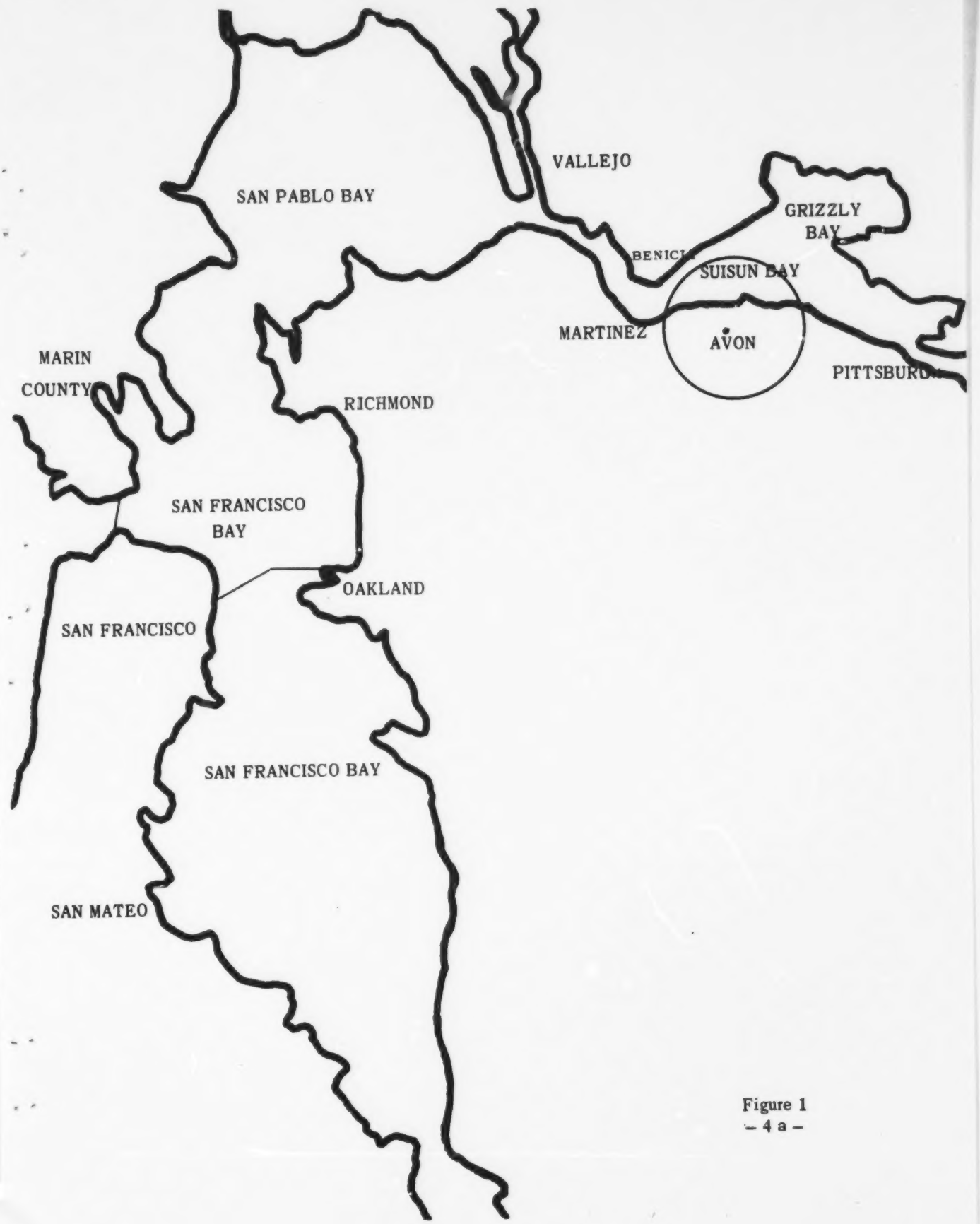
VALLEJO
SAN PABLO BAY
GRIZZLY
BAY
BENICIA
SUISUN BAY
MARTINEZ
AVON
PITTSBURG
MARIN
COUNTY
RICHMOND
SAN FRANCISCO
BAY
OAKLAND
SAN FRANCISCO
SAN FRANCISCO BAY
SAN MATEO

Figure 1

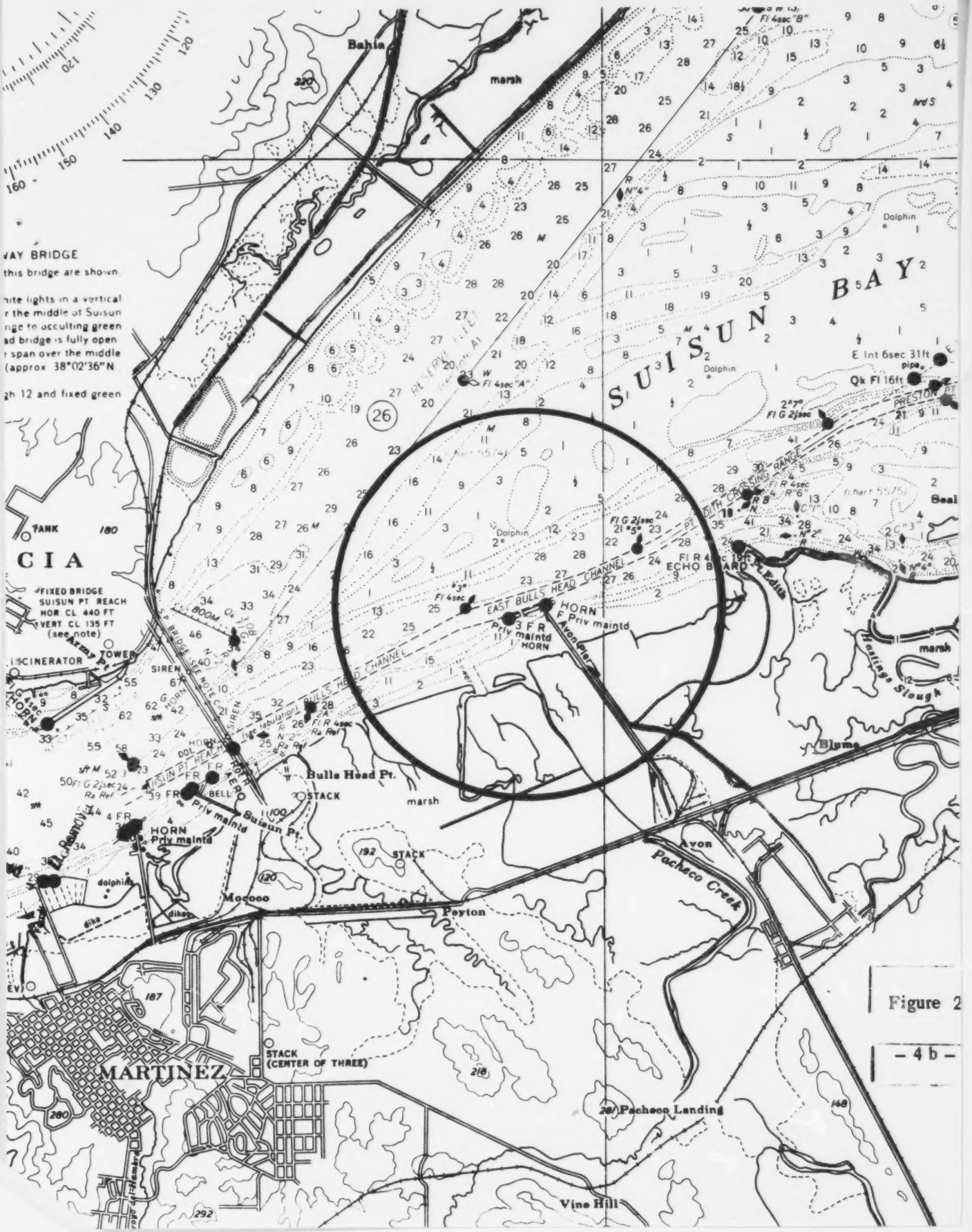
Bahia
marsh
SUISUN BAY
Dolphin
E Int 6sec 31ft
pipe
Qk Fl 16ft
PRESTON PT
Fl G 2½sec
Fl 4sec "A"
Fl 4sec "B"
26
EAST BULLS HEAD CHANNEL
Fl 4sec
3 F R
Priv maintd
HORN
F Priv maintd
Avon Pier
Seal
Hastings Slough
marsh
Blums
Bulls Head Pt.
STACK
marsh
SUISUN PT REACH
FIXED BRIDGE
SUISUN PT REACH
HOR CL 440 FT
VERT CL 135 FT
(see note)
INCINERATOR
TOWER
SIREN
Fl R 4sec
Ra Ref
Priv maintd
Suisun Pt.
HORN
Priv maintd
dolphins
dike
Mococo
Peyton
Avon
Pacheco Creek
STACK
STACK (CENTER OF THREE)
MARTINEZ
Pacheco Landing
Vine Hill
WAY BRIDGE
this bridge are shown
nite lights in a vertical
r the middle of Suisun
nge to occulting green
ad bridge is fully open
span over the middle
(approx 38°02'36"N
gh 12 and fixed green

Figure 2

In adopting Resolution No. 576, "Prescribing Requirements as to the Nature of Twelve Discharges by Phillips Petroleum Company From its Avon Refinery Into Suisun Bay, Walnut Creek and Hastings Slough, and Onto Land, at Points Near Avon, Contra Costa County," July 16, 1964, the San Francisco Bay Regional Water Quality Control Board established the beneficial uses of the waters of Suisun Bay (and adjoining water-bodies and watercourses) as:

1. A seasonal source of domestic water supply at Army Point and at Mallard Slough during periods of relatively high stream flow;
2. Small boat harbors;
3. A migration route for the spawning runs of salmon, shad, steelhead and striped bass;
4. The propagation of fish and aquatic life;
5. Sport fishing;
6. A source of industrial process and cooling water;
7. Pleasure boating; and
8. Navigation.

It is anticipated the above listing also covers all future and potential uses of the waters of Suisun Bay, in the vicinity of the Phillips Petroleum Company waste discharge.

Within the general group of beneficial uses of the waters of the Bay, those concerned with the migration route for the spawning runs of cold water game fish; propagation of fish and aquatic life; and sport fishing, have been selected as being of critical importance in the need for protection.

Water quality criteria for selected parameters in the receiving waters of Suisun Bay, California, within the vicinity of the waste discharge from the Avon Refinery, Phillips Petroleum Company, Contra Costa County, California, are presented herein. The criteria are based on the need to enhance the quality of water in the Bay.

WATER QUALITY PARAMETERS AND CRITERIA

Selected parameters and correlative water quality criteria (as numerical values) are presented below. Unless otherwise noted, criteria values are those levels of concentration which must not be exceeded in the receiving waters of the Bay.

Parameter	Criteria
Sulfides	0.1 mg/l
Ammonia	0.1 mg/l
pH Value	Not less than 7.3 nor greater than 8.3.
Dissolved Oxygen	Not less than 85% of saturation, or 5.0 mg/l - whichever is greater.
Phenols	0.03 mg/l
Total Oils	15.0 mg/l in the waste effluent and will not: (a) produce oily films or floating oil in quantities great enough to cause iridescence on the surface of the receiving waters; or (b) produce oil deposits on the bottom or shoreline of Suisun Bay in the vicinity of the waste discharge.
Toxic Substances	None - no substance, or combination of substances, in concentrations which are deleterious to fish or aquatic life, shall be discharged to the waters of Suisun Bay.

Staff time limitation made it necessary to restrict consideration of parameters to the above listing. Inclusion of a parameter was based on past experience -- and is an indication of the importance attached

to these constituents in so far as their adverse effect on the aquatic environment. Had time permitted, consideration would have been given to these additional parameters:

1. Temperature
2. Heavy Metals
    a. Chromium
    b. Copper
    c. Lead
    d. Zinc
3. 5-Day, 20°C BOD
4. Settleable Solids
5. Total Suspended Solids
6. MPN Coliform

The omission of these parameters from this report should not be construed as limiting the need for their consideration. Local and State water pollution control agencies should include them in their regulatory requirements.

RATIONALE FOR WATER QUALITY CRITERIA

General

The water quality criteria recommended for the waters of Suisun Bay in the vicinity of the waste discharge of the Avon Refinery, Phillips Petroleum Company, are based on present knowledge and experience of the effects on fishes and allied aquatic forms when non-toxic and toxic substances are introduced into the aquatic environment. There is much to be learned -- as microanalytical-toxicological methods are improved, our assessment of the effects of wastes on aquatic life will be more definitive. The criteria presented herein are a beginning -- a step forward in our understanding of what is needed to protect our irreplaceable natural resources. As additional facts are discovered, as analytical techniques are improved, the criteria will be revised as indicated. The rationale supporting the criteria for the selected parameters follows.

SULFIDES

The relation of the sulfide parameter to toxicity on aquatic life is based on the concentration of the undissociated (un-ionized) hydrogen sulfide molecule in the receiving water. The degree of toxicity is related directly to the pH; the lower the pH, the greater the number of undissociated molecules -- and the greater the toxicity. The magnitude of this pH relationship is represented by figures extracted from Table 27, Hydrogen Sulfide Factors, page 428, Standard Methods.[1/]

Hydrogen Sulfide Factors

pH	Factor	pH	Factor
5.0	0.98	8.0	0.048
6.0	0.83	8.3	0.025
7.0	0.33	8.4	0.020
7.3	0.23	9.2	0.0032
7.5	0.14	9.6	0.0013

Water Quality Criteria[2/] discusses the effects of hydrogen sulfide on fish and other aquatic life on page 200. Dr. Tarzwell, although indicating the allowable amounts of undissociated sulfides are not well

---

1/ Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 12th Edition, 1965.

2/ Publication No. 3-A, California State Water Quality Control Board, 2nd Edition, McKee and Wolf, 1963.

established for sea water, states available literature points to an upper limit of 0.1 mg/l. Dr. Jones[1/] supports an even lower limit of undissociated hydrogen sulfide molecule -- the toxic effect being maintained below 1.0 mg/l and the linear portion of the fatality curve indicating a threshold concentration of 0.05 mg/l.

The toxic level of several of the parameters under consideration is affected by the pH of the receiving waters. Additional comments on the interrelationship of pH and the respective parameter are presented under the item "pH" as well as under the parameter affected.

Water Quality Criteria Value

The concentration of the undissociated hydrogen sulfide molecule (H_2S) shall not exceed 0.1 mg/l in the receiving waters.

1/ Fish and River Pollution, Jones, J. R. Erichsen, Butterworths, 1964.

AMMONIA

The toxicity of ammonia to aquatic life is related directly to the concentration of the undissociated form of the base. Past terminology has identified this base form as the undissociated ammonium hydroxide (NH_4OH) molecule; current practice[1/] indicates the predominant species in these solutions is actually NH_3 where the equilibrium is represented as,

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The toxicity of the undissociated form of the base is dependent upon the pH, temperature and concentration of other ions in the receiving waters. According to Water Quality Criteria, the ratio of ammonium ions to the undissociated form of the base varies with the pH as follows:

Ratio Of Ammonium Ions
To Undissociated Form Of
The Base At Varying pH

25°C

pH	NH_4^+	Undissociated Form of the Base
6.0	1800	1
7.0	180	1
7.3	90.2	1
8.0	18	1
8.3	9.02	1
9.0	1.8	1
9.2 or 9.3	1	1

1/ Analytical Chemistry: An Introduction, Skoog, Douglas A., and West, Donald M., Hott, Rinehart and Winston, 1965.

As the pH of a solution approaches 9.3, an equal number of (NH_4^+) ions and undissociated ammonium hydroxide molecules (NH_4OH) are present -- and maximum toxicity results. The ratios for pH values of 7.3 and 8.3 were calculated using a dissociation constant of 1.8×10^{-5} (25^oC).

The dissociation constants for 10^oC (expected temperature of Suisun Bay water) and 25^oC are 1.57×10^{-5} and 1.77×10^{-5} respectively. The effect of temperature, consequently, will be relatively unimportant.

The effect of ionic strength in quantitative terms, an equilibria, is called the <u>activity</u> of the substance. The action of other ions in a solution tend to set up barriers of opposite charges around the dissociated ions of the subject substance -- thereby making the recombination (undissociated form) more difficult. The phenomena is described on page 25 of the Skoog and West reference. The total effect is the production of <u>less</u> quantities of undissociated molecules where other ions are in solution (such as brackish or saline waters) than if the substance was being introduced into an aqueous solution in which there were no other ions than those of the solute. This phenomena may explain the apparent lack of ammonia toxicity due to some waste discharges to brackish water in the San Francisco Bay area.

Water Quality Criteria discusses the effects of ammonia on fish and other aquatic life on page 133. Other literature references studied by Dr. Tarzwell indicate there are adverse effects of the undissociated ammonium hydroxide molecule at concentrations of 0.3 mg/l.

There is an interdependent relationship between the dissolved oxygen (DO) content of receiving waters and the concentration of carbon dioxide (CO_2) at the gill surface -- where ammonia toxicity is concerned. Water Quality Criteria states:

> "The toxicity of ammonia to fish is increased markedly at low tensions of dissolved oxygen .... The concentration of excreted carbon dioxide at the gill surface varies with the oxygen content of the water; hence, as the oxygen tension is reduced, the concentration of excreted CO_2 is also reduced and the pH value of the water in contact with the gill surface rises, leading to an increased toxicity of an ammonia solution."

The Federal Water Pollution Control Administration's Central Pacific River Basins Comprehensive Water Pollution Control Project is currently conducting studies of San Francisco Bay and the Sacramento-San Joaquin Delta which will lead to information on the effects of increased nitrogen and phosphorus levels on the beneficial uses of the Bay waters. Recommendations will be made concerning water quality standards which should be adopted to protect the stated beneficial uses. Since ammonia is an important fraction of the constituents making up the total nitrogen concentration in the Bay, it may be necessary to revise the allowable ammonia level recommended in this report.

Limited data available on concentrations of total nitrogen existing in Bay waters in the vicinity of the Phillips Petroleum Company discharge, show values ranging from approximately 0.5 to 2.0 mg/l as N. The ammonia nitrogen (NH_3-N) fractions of the total nitrogen range from 0.1 to 0.7 mg/l.

The "Report of Water Quality Criteria, Calumet Area-Lower Lake Michigan," January, 1966, establishes the following limits on ammonia reported as nitrogen for waters representing study areas where fish and wildlife propagation is to be protected as a beneficial use:

	NH_4-N (mg/l)	
Area	Annual Average	Single Daily Value or Daily Average
Open Water	0.02	0.05
Inner Harbor Basins	0.05	0.12
Shore Water	0.05	0.12
Wolf Lake	0.05	0.12

Water Quality Criteria Value

The concentration of the undissociated ammonium hydroxide molecule (NH_4OH) shall not exceed 0.1 mg/l in the receiving waters.

pH* VALUE

Control of the pH range in the receiving waters of Suisun Bay, to minimize adverse effects on aquatic life, depends upon several factors:

1. Temperature;
2. Dissolved oxygen;
3. Prior acclimatization to a specific pH level;
4. Concentration of various anions and cations; and
5. Salinity.

Temperature is an interrelated, rather than specific, factor in the effects of pH on aquatic life. Elevation of temperature in the receiving waters increases the toxicity of many substances; a simultaneous adverse pH value and rise in temperature magnifies the toxicity of these substances.

A decrease in pH adversely affects the ability of fishes to extract DO from the aquatic habitat. This may be related to an increase of the carbon dioxide level in the water (in the presence of sufficient quantities of carbonates) when the pH value is decreased.

---

* The symbol "pH" is used to designate the logarithm (base 10) of the reciprocal of the hydrogen-ion concentration. Thus, if $(H^+) = 10^{-5}$ mols per liter, then pH = 5.

The University of California, Berkeley, California, reported[1/] a pH range from 7.3 to 8.3 (mean of 7.6) for the waters of the Suisun-San Pablo Bay complex in 1962-1963. Nicol[2/] (page 13) indicates sea water in equilibrium with the atmosphere has a normal pH value of 8.1. Sverdrup, et al.[3/] (pages 195, 209) state where sea water is in equilibrium with the CO_2 in the atmosphere, the pH is between 8.1 and 8.3 -- depending upon the temperature and salinity of the water. Anadromous fishes using waters of the Pacific Ocean and Suisun Bay as part of their aquatic environment have become acclimated to sea and brackish water having a general pH range from 7.6 to 8.3.

Under any given set of equilibria the following forms of CO_2 can exist in sea water:

$$CO_2\text{(dissolved)} \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^-\text{(bicarbonate)} \rightleftharpoons CO_3^-\text{(carbonate)}$$

If a strong <u>acid</u> is added to sea water, the equilibria is displaced toward the free CO_2; if an <u>alkaline</u> substance is added, the equilibria is shifted toward the carbonate. Nicol[4/] and Sverdrup, et al.[5/] agree

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1/ "A Comprehensive Study of San Francisco Bay, 1962-63," Sanitary Engineering Research Laboratory, College of Engineering and School of Public Health, University of California, Berkeley, California, SERL Report No. 64-3.

2/ "The Biology of Marine Animals," Nicol, J. A. Colin, 1960.

3/ "The Oceans," Sverdrup, H. U.; Johnson, Martin W.; and Fleming, Richard H., 1942.

4/ Ibid., page 9.

5/ Ibid., page 173.

the average composition of sea water includes approximately 1400 mg/l of HCO_3^-. The addition of an acid waste to water containing this amount of bicarbonate will promote the production of free CO_2 -- a factor in fish toxicity. Water Quality Criteria indicates the following ratios between carbonic acid (H_2CO_3) and bicarbonate ions (HCO_3^-) at various pH values:

pH	Ratio	Factor
8.0	0.0286	1
7.0	0.86	30
6.0	2.86	100

When a factor of unity is assigned to the ratio at pH 8.0, the ratio at pH 6.0 assumes a relative magnitude of 100 -- a hundredfold increase in the ratio of carbonic acid and bicarbonate ions for a decrease of two units of pH value.

Water Quality Criteria discusses the effects of pH on fish and other aquatic life on page 236.

The interrelationship of the toxicity of substances found in petroleum industry wastes and the pH of the media has been noted:

1. Sulfides - the lower the pH, the greater the toxic effects; and
2. Ammonia - the higher the pH, the greater the toxicity.

Water Quality Criteria Value

The waste discharge shall not cause the pH value of the receiving waters to be less than 7.3 or greater than 8.3.

DISSOLVED OXYGEN

Dissolved oxygen (DO) requirements for sustaining healthy aquatic life, especially fish, are dependent upon:

1. Age and species of the fish;
2. Temperature of the water;
3. Concentration of salts in the aquatic environment; and
4. Prior acclimatization to a specific dissolved oxygen level.

In Suisun Bay the major sport fishes are the salmonids (salmon, steelhead trout) and striped bass. These fishes are found in a complete range of sizes from fry to mature adult. Locally, both salmonids and striped bass are known as cold water fishes.

The life cycle of these anadromous fishes is such that relatively fresh water is necessary for the egg-laying and egg-hatching processes. The cycle begins in fresh water; there is a migration to either bay or open ocean; a return to essentially the same area of their birth for the completion of the cycle. The entire cycle on the Pacific Coast takes place in cold waters having dissolved oxygen concentrations of roughly 85 per cent of saturation. For salinities from 0 to 12,000 mg/l of chlorides, and temperatures ranging from 10° to 20°C, the fish are acclimated to waters having DO concentrations varying from 7.0 to 9.5 mg/l.

Under the discussion for AMMONIA, the increase of toxicity of ammonia due to decreases in oxygen tension was described. Similar increases in toxicity of substances such as excessive dissolved carbon dioxide,

cyanides, zinc, lead, copper or cresols, where low concentrations of dissolved oxygen exist, are mentioned in Water Quality Criteria.

Dr. Tarzwell's experience with warm water fishes indicates minimum dissolved oxygen content should be 4.0 mg/l. Commenting at length on the factors affecting DO requirements for fish, he concluded a higher DO concentration for the sport fishes found in Suisun Bay was warranted.

Water Quality Criteria Value

The waste discharge shall not cause the dissolved oxygen (DO) content of the receiving waters to be less than 85 per cent of saturation or 5.0 mg/l -- whichever value is greater.

PHENOLS

According to Water Quality Criteria, phenolic compounds may affect fish in two ways:

1. By a direct toxic action; and
2. By imparting a taste to fish flesh.

Since it takes considerably higher concentrations (in excess of 0.2 mg/l) to produce toxic reactions in fish life, the "flesh tainting" concentration may well be the controlling factor for this parameter.

Teal[1/] indicates as a well-known fact, fish will absorb odor compounds from water; additionally, these accumulate in the flesh and may cause a noticeable change in the odor of the flesh; some organic compounds in concentrations below olfactory detection may concentrate in the tissue and produce an odor far greater than the water itself; and many of these organic compounds are additive in characteristics and two or more of them in concentrations below their individual taste thresholds can combine to produce taste in fish. The manuscript contains a table of fish taste thresholds as established by experienced, perceptive tasters.

1/ "The Control of Waste Through Fish Taste," Teal, James L., The Dow Chemical Company, American Chemical Society, National Meeting, 1959.

Table of Fish Taste Thresholds Determined at Dow

Compound	Taste Threshold (ppm)
Phenol	1.0
O-sec. butyl phenol	0.3
P-tert. butyl phenol	0.03
O-phenylphenol	1.0
O-chlorophenol	0.015
P-chlorophenol	0.05
2,4 dichlorophenol	0.005
DiphenylOxide	0.05
Acetophenone	0.5
Styrene	0.25
Alpha methyl styrene	0.25
Isopropylbenzene	<0.25
Ethyl benzene	<0.25
B,B'-dichlorodiethylether	1.0
O-dichlorobenzene	0.25
Toluene	0.25
Cresylic acid (meta-para)	0.2
Kerosene	0.1
"Insecticide" oil (heavy aromatic naphtha)	0.2
"Cutting" oil (emulsifiable	>15.0

Water Quality Criteria Value

The concentration of phenols shall not exceed 0.03 mg/l in the receiving waters.

TOTAL OILS

The discharge of oils or oily wastes to a receiving water activates a separation process for these petroleum wastes. The lighter fractions become floating oils or oily films; the heavier fractions (heavier-than-water oils) are deposited on the bottom or are washed ashore on beaches (as are some of the floating oils); or the oil dissolves or emulsifies in the water solute and remains in the main body of water.

Water Quality Criteria indicates oily substances interfere with aquatic life by:

1. Coating the gills of fish to restrict or prohibit adequate respiratory action;
2. Destruction of algae and other plankton by freely floating oil or oil emulsions thereby removing a source of fish food;
3. Coating the bottom of the aquatic area resulting in the destruction of benthic organisms (also fish food) -- and interfering with spawning areas;
4. Tainting the flavor of fish flesh through ingestion of soluble and emulsified fractions;
5. Deoxygenation of waters by oily organics resulting in fish kills;
6. Interfering with the natural processes of reaeration and photosynthesis; and

7. Toxic effect of water-soluble fractions on fish or fish food organisms.

Both Rosen[1/] and Black refer to the Report of the International Joint Commission on the Pollution of Boundary Waters, 1951, which set as one of its objectives (p. 19):

CHEMICAL WASTES -- OTHER THAN PHENOLIC

"Adequate protection should be provided if:

(e) Oils and floating solids are reduced to a point such that they will not create fire hazards, coat hulls of water craft, injure fish or wildlife or their habitat, or will adversely affect public or private recreational development or other legitimate shoreline developments or uses. Protection should be provided for these waters if plant effluents or storm water discharges from premises do not contain oils, as determined by extraction, in excess of 15 ppm, or a sufficient amount to create more than a faint iridescence."

Rosen also indicates:

1. Water-soluble non-hydrocarbon components of oily discharge may be more toxic than the emulsified oil portion; and
2. The effective level causing damage to fish taste must be considered.

1/ Dr. Aaron A. Rosen, Chemist, Organic Contaminants Unit, Chemistry and Physics Activities, Division of Research and Development, Federal Water Pollution Control Administration, U. S. Department of the Interior, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio.

Neumann, et al.[1/] in reviewing the planning and ultimate operation of the Shell Oil Company plant at Anacortes, Washington, concluded maximum efforts must be made to protect wildlife resources and adjoining property in operating the refinery. By provision of API-type oil-water separators, flocculating agents followed by primary clarifiers -- and final biological treatment (trickling filter and activated sludge processes) -- the Company was able to produce an effluent containing only 7.0 mg/l of oil. The State of Washington had previously set 15.0 mg/l as the maximum limit.

The Richmond refinery, Standard Oil Company of California, produces an effluent containing from 8.0 to 15.0 mg/l[2/] of oil through use of API oil-water separators followed by a series of biological oxidation ponds. The current discharge requirements (San Francisco Bay Regional Water Quality Control Board) set a maximum limit of 30.0 mg/l for grease -- with a 10.0 mg/l average for samples taken during any three consecutive months.

Water Quality Criteria Value

The plant effluent discharged to the waters of Suisun Bay shall not:

1. Produce oily films or floating oil in quantities great enough to cause iridescence on the surface of the receiving waters;

1/ "Waste Disposal at Anacortes," Neumann, E. D.; Reno, C. J.; and Burroughs, L. C., Shell Oil Company, The Oil and Gas Journal, May 19, 1958.

2/ Telephone communication, Hayse Black with John Easthagen, Staff Engineer, Chevron Research Company, Richmond, California, November 23, 1965.

2. Produce deposits on the bottom or shoreline of Suisun Bay in the vicinity of the waste discharge; and

3. Contain in excess of 15.0 mg/l of total oils.

TOXIC SUBSTANCES

Water Quality Criteria does not consider "toxic substances" as a classification; rather each potentially toxic material is treated separately. The phrase as used herein refers to those parameters, or combination of parameters, for which specific criteria values are either unknown or not easily defined. The enormous number of chemical compounds found in current industrial waste discharges, along with the complex interaction of these chemicals -- one with the other, and with other compounds already in the receiving water -- render it virtually impossible to set water quality criteria values for each chemical.

To ignore the possible detrimental effects of these chemicals on the aquatic environment, however, would negate much of the water pollution control advances already accomplished. To take them into consideration, the physical scientist has devised a measuring technique called a bioassay. Two major types of bioassay are used:

1. Continuous Flow Bioassay in which test fish, of a species normally found in the receiving waters under study, are continuously exposed (flow-through) to a mixture of the waste discharge and the receiving water (proportioned on the calculated dilution factor of the effluent in the receiving water) -- and the mortality rate of the test fish is compared with that of the same species of fish exposed to the receiving water alone.

2. Static Bioassay in which test fish, of a species normally found in the receiving waters under study, are exposed to various concentrations of the waste effluent. A separate tank is used for each concentration of the waste. The recommended index of relative acute toxicity is the median tolerance limit (TL_m) -- the concentration of test material at which just 50 per cent of the test animals survive for a specified period of exposure, usually 96 hours.

Water Quality Criteria recognizes the toxicity of potential pollutants in water toward plant and animal life as a time-concentration phenomenon -- "acute" or "direct" toxicity being the lethal action within a period of 96 hours, or less; the "chronic" toxicity being those deleterious effects which may not be evident for weeks, months or longer. The static bioassay would reveal the acutely toxic wastes; the continuous technique would relate to changes in appetite, metabolism, disorders of the nervous system, reproduction or even the long-time mutation of genes.

Henderson and Tarzwell[1/] review the concepts of using bioassays for determining the toxicity of wastes and provide extensive detail on what

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1/ "Bio-Assays For Control of Industrial Wastes," Henderson, Croswell and Tarzwell, Clarence M., 12th Purdue Industrial Wastes Conference, Purdue University, Lafayette, Indiana, May 13-15, 1957.

to provide in facilities and equipment for a testing program. Dorris, et al.,[1/] under a grant from the Oklahoma Oil Refiners' Waste Control Council, were among the early investigators to recognize that toxicity rather than oxygen demand was the most important effect of oil refinery effluents on receiving waters. Their work was done entirely with Oklahoma refineries.

Water Quality Criteria Value

None

To preclude the discharge of any substance, or combination of substances, to the waters of Suisun Bay, in concentrations which are deleterious to fish or aquatic life, the discharger shall perform, at his option, either of the following bioassays:

1. Continuous flow bioassay in which the survival of test fish will compare favorably with those which survive in a control tank supplied with water directly from Suisun Bay. As operating data is accumulated, the range (possibly from 10 to 30 per cent) within which the survival rates match can be established.

2. Static bioassay in which the 96-hour TL_m of the waste effluent will be determined. The discharger will then provide sufficient

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1/ "Toxicity Bioassay of Oil Refinery Effluents in Oklahoma," Dorris, Troy C.; Gould, William; and Jenkins, Charles R., 3rd Annual Water Disposal and Stream Pollution Conference of the Western Petroleum Refiners Association, Wichita, Kansas, October 1-2, 1958.

dilution water before and/or during discharge to the receiving waters so as to reduce the TL_m concentration to one-tenth of the bioassay value.

ANALYTICAL PROCEDURES

Analytical procedures used to determine the criteria values of the selected parameters must be those generally recognized as proven techniques for the specific parameter under consideration. In the United States these procedures are prepared and published jointly by the American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Pollution Control Federation (WPCF) under the title, "Standard Methods for the Examination of Water and Wastewater". The Twelfth Edition was published in 1965 -- technical persons refer to the publication as "Standard Methods". Unless otherwise noted, analytical techniques referenced in this report will refer to this publication.

The toxic concentration making up the water quality criteria values for certain parameters is less than 1.0 mg/l. As parameter concentrations drop below this level, analytical procedures become less accurate -- and often do not have a high degree of reproducibility. Unless noted, criteria values have been set for the receiving waters of Suisun Bay. Recognizing the difficulty (as noted above) both discharger and surveillance agencies would have in analyzing the receiving water for some parameters, in specific instances the criteria value has been calculated for the waste effluent prior to discharge to Suisun Bay. The dilution afforded the wastes by the proposed deep water, pumped waste discharge point allows a higher value for the criteria; in many cases enough higher

as to make analytical procedures in Standard Methods applicable. Where this calculation has been used, the procedural steps are explained under the specific parameter heading.

Sulfides

The general discussion of sulfides begins on page 426, Standard Methods -- with the analytical procedure (B. Colorimetric Method) for dissolved sulfides presented on page 429. The test is especially recommended for low sulfide concentrations and is applicable in the range of 0.05 to 20 mg/l.

The procedure for calculating the concentration of undissociated (un-ionized) hydrogen sulfide molecules is found on page 428 -- Table 27 providing the multiplication factors for a pH range of 5.0 to 9.6.

In the analytical procedure the technician will be testing for dissolved sulfides ($S^{=}$). The criteria value of 0.1 mg/l refers, however, to the toxic form, the undissociated hydrogen sulfide (H_2S) molecule. The maximum allowable value of the undissociated molecule will occur at pH 7.3, as established in the SULFIDES and pH sections of this report.

Calculations

($S^{=}$) x Hydrogen Sulfide Factor = Concentration of Un-ionized Hydrogen Sulfide

Therefore, at pH 7.3 --

($S^{=}$) x 0.23 = 0.1 mg/l (H_2S) and ($S^{=}$) = 0.4 mg/l

In practice then, the technician would be checking the receiving waters for dissolved sulfides ($S^{=}$). At the lowest pH allowed (7.3), if tests indicate a ($S^{=}$) concentration of 0.4 mg/1 or less, the discharge would be in compliance with the criteria value for undissociated hydrogen sulfide (H_2S) molecule. Comparable allowable dissolved sulfide ($S^{=}$) concentrations with pH ranging from 7.4 to 8.3 are listed below:

pH	Dissolved Sulfide ($S^{=}$) Concentration (mg/1)
7.4	0.59
7.5	0.71
7.6	0.91
7.7	1.10
7.8	1.37
7.9	1.70
8.0	2.08
8.1	2.50
8.2	3.23
8.3	4.00

Ammonia

Analytical procedures for Nitrogen (Ammonia) begin on page 389, Standard Methods. Method B, page 391, (Distillation followed by Nesslerization) is the mandatory procedure.

In the analytical procedure the technician will be testing for ammonia nitrogen. This analysis would include both ammonium ions (NH_4^+) and undissociated ammonium hydroxide (NH_4OH) molecules. It is necessary, then, to relate the allowable (0.1 mg/1 at pH 8.3 as established in the AMMONIA section) concentration of the undissociated ammonium hydroxide (NH_4OH) molecule to the comparable concentration of ammonia nitrogen, as tested.

Calculations

Convert 0.1 mg/l (NH_4OH) to nitrogen (N)

$$\frac{N}{(NH_4OH)} \times 0.1 \text{ mg/l} = 14/35 \times 0.1 = 0.04 \text{ mg/l as N}$$

At pH 8.3 the ratio of $\frac{(NH_4^+)}{(NH_4OH)} = 9.02$ as indicated in the section on AMMONIA.

Thus for every molecule of (NH_4OH) there are 9.02 ions of (NH_4^+) -- and the same ratio applies to nitrogen (N) in these forms.

Thus the concentration of (NH_4^+) as (N) in the receiving waters is --

$9.02 \times 0.04 = 0.361$ mg/l as N

and the total allowable ammonia nitrogen [(NH_4OH) and (NH_4^+)] as nitrogen (N) is --

0.361 mg/l + 0.04 mg/l = 0.40 mg/l

Applying the dilution factor afforded by the deep-water discharge point (7 to 1), we have --

0.40 mg/l x 7 = 2.8 mg/l, at pH 8.3

as the maximum allowable concentration of ammonia nitrogen, as nitrogen (N), in the waste effluent, equated to 0.1 mg/l of undissociated ammonium hydroxide (NH_4OH) molecule in the receiving waters. If the technician finds 2.8 mg/l or less in the effluent when the pH of the receiving waters is 8.3, the discharge is in compliance. Allowable ammonia nitrogen, as nitrogen (N), can be calculated for other pHs down to and including 7.3.

pH Value

The general discussion of pH value begins on page 225, Standard Methods -- the analytical procedure (Glass Electrode Method) is presented on page 226. With proper care, an accuracy of 0.1 pH units may be obtained with AC line-operated instruments.

For compliance the pH should not range below pH 7.3 or above 8.3 in the receiving waters.

Dissolved Oxygen

The general discussion of oxygen (dissolved) begins on page 405, Standard Methods -- with the analytical procedure (A. Azide Modification of Iodometric Method) presented on page 406. Interference by various ions and compounds is minimized by this modification of the basic iodometric method; accuracy is approximately 0.1 mg/l.

Table 25 - Solubility of Oxygen in Water Exposed to Water-Saturated Air, page 409, Standard Methods, lists saturation solubilities of oxygen in waters containing various chloride concentrations at different temperatures. The Table can be used to obtain the saturation value at the time of sampling. For compliance the dissolved oxygen content of the receiving water must be 85 per cent of saturation or 5.0 mg/l -- whichever value is greater.

Phenols

The general discussion on phenols begins on page 514, Standard Methods -- with the generally preferred analytical procedure (A. Chloroform Extraction Method - preceded by Distillation) presented on pages 516-517. The testing

procedure is extremely sensitive so is adaptable for use in waste waters containing less than 1.0 mg/l phenol.

Calculations

Applying the dilution factor afforded by the deep-water discharge point (7 to 1), we have --

0.03 mg/l x 7 = 0.21 mg/l

If the technician can demonstrate a phenol concentration of 0.21 mg/l or less in the waste effluent prior to discharge to the waters of Suisun Bay, the discharge will be in compliance.

Total Oils

The discharger is given a choice between two analytical procedures for the determination of total oils in the waste effluent. These are:

1. American Petroleum Institute Method 732-53 (1957), "Determination of Non-Volatile Oily Material," (Flocculation, Extraction, U-Tube Method); or
2. Standard Methods determination for Grease.

The discussion on Grease begins on page 383, Standard Methods -- with the analytical procedure (A. Soxhlet Extraction Method) appearing on page 384. The procedure is reported to be accurate within 1.0 mg/l for both vegetable oil and petroleum products.

The technician will be testing the waste effluent -- in the absence of oily films, floating oil or oily bottom deposits in the receiving waters -- thus a determination of 15.0 mg/l or less of total oils will be in compliance with discharge requirements.

Toxic Substances

The discharger is given a choice between two analytical procedures for the determination of toxic substances:

1. Static bioassay; and
2. Continuous flow bioassay.

The discussion on Bioassay Methods begins on page 545, Standard Methods -- the analytical procedure (Routine Bioassay Method) is presented on page 546.

Static Bioassay

Calculations

Henderson and Tarzwell[1/] compute the dilution water required to reduce the toxicity of the total flow or volume of the waste effluent to 50 per cent mortality of the test fish by using the following formula:

$$\text{Dilution Volume} = \frac{100-TL_m}{TL_m} \times \text{Effluent Flow}$$

This value can be in any convenient unit -- cubic feet per second (cfs), million gallons per day (mgd), etc. -- and gives a direct measure of the toxicity contributed by the effluent.

Since this dilution volume will only provide for survival of 50 per cent of the fish, additional

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1/ Ibid., page 1014

dilution is needed to produce an effluent which will have no detrimental effect on aquatic life in the receiving waters. This is accomplished by use of an "application factor", a whole number by which the above calculated dilution volume may be multiplied to give the total dilution water requirement for safety to aquatic life.

Then --

Dilution Volume x Application Factor = Total Dilution Flow Needed

In the absence of contrary evidence as to its applicability, an application factor of 10 has been generally recognized as appropriate to use for industrial wastes in the United States.

Continuous Flow Bioassay

The general procedure for continuous flow bioassay has been explained in the section on TOXIC SUBSTANCES. Two industrial firms have reported using this technique -- we would anticipate their technical staffs would be pleased to discuss operational procedures with officials at Phillips.

1. Esso Standard Oil Company
   Post Office Box 551
   Baton Rouge, Louisiana

2. E. I. DuPont De Nemours & Company, Inc.
   Electrochemical Department
   Niagara Falls, New York

   Attention: Mr. George R. Amery

DEEP-WATER EFFLUENT

DIFFUSION BY PUMPING

In reconsidering an original plan for a combination gravity, deep-water discharge and an onshore overflow facility, Phillips has proposed instead a deep-water, pumped waste discharge at the 45-foot depth off the face of the Avon Pier. The proposal, "Report to Tidewater Oil Company Upon Effluent Diffusion by Pumping," March 1966, was prepared by Metcalf & Eddy Engineers, 2500 El Camino Real, Palo Alto, California.

A review of the proposal indicates the consultants have used an approach generally recognized as applicable to a submerged discharge. The jet trajectory was established using the theory of Cooley and Harris -- the diffusion by tidal movement was based on work done by Brooks. Table 2, Concentration and Dilution of Wastes (page 5), lists the following dilution of combined wastes (East Canal plus effluent from the oxidation pond) through use of pumped discharge:

	Flow (gpm)	
Dilution	17,400	14,600
Maximum	36:1	33.5:1
Average	11.6:1	10.6:1
Minimum	7.4:1	6.7:1

In selecting a dilution factor to apply to the waste effluent as it is dispersed in the receiving waters, we must select the conditions when minimum dilution is afforded. This minimum dilution occurs when the

flow is 14,600 gpm -- and the ratio is 6.7:1. On the basis of this data we have selected a dilution ratio of 7 to 1.

As for dilution, we must select the minimum width of plume in establishing the outer physical limits of the "mixing zone" at the point of discharge. This would approximate conditions at slack tide, when minimum dilution takes place. The width of the plume with a flow of 14,600 gpm is 27.1 feet. We recommend a "mixing zone" with an arbitrary diameter of 50 feet -- with the center located 62 feet from the face of the wharf, directly in line with the point of discharge.

The proposal for a deep-water, pumped waste effluent discharge is well taken. We support this concept as being in the best interests of a practical solution to the waste discharge problem.

MONITORING PROGRAM

The establishment of water quality criteria for the receiving water of Suisun Bay in the vicinity of the waste discharge point for the Phillips Petroleum Company carries with it the responsibility of monitoring these waters, and the effluent waste discharge stream, for compliance with the criteria.

In the introduction to the ANALYTICAL PROCEDURES section a point was made of the difficulties involved for both discharger and surveillance agencies in measuring the receiving water for some parameters. It was noted the analytical procedures, in some cases, become less accurate when concentrations of substances to be identified are less than 1.0 mg/l. To minimize these difficulties the discharger is asked to monitor both the receiving water and the effluent waste stream; the table below indicates the monitoring point for the selected parameters.

Parameter	Monitoring Point
Sulfides	Receiving Water
Ammonia	Effluent Stream
pH Value	Receiving Water
Dissolved Oxygen	Receiving Water
Phenols	Effluent Stream
Total Oils	Receiving Water & Effluent Stream
Toxic Substances	Effluent Stream

To assure complete mixing of the two major waste streams (effluent from the oxidation pond and flow in the East Canal), effluent samples should be collected as near the end as is practical of the discharge line on Avon Pier. The discharger should conduct sufficient inplant, oxidation pond influent and effluent stream analyses to assure maximum control of processes and water pollution control system efficiency.

The hydraulics of the deep-water, pumped waste effluent discharge led to the adoption of the 50-foot diameter "mixing zone". Receiving water criteria must be met at points no farther than 25 feet from the center of the rising waste plume, the center of which has been calculated to be 62 feet from the face of Avon Pier at periods of slack tide. For those analyses scheduled for the waste effluent stream, the discharger will be afforded a 7 to 1 dilution factor in relating the parameter concentration to the receiving waters.